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FILING DATE: *September 12, 2003*

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Certified by



Jon W Dudas

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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

DETERRING THE FORMATION OF CRYSTALLINE HYDRATES IN GAS AND OIL SYSTEMS

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ENCLOSED APPLICATION PARTS (check all that apply)

Specification Number of Pages

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Other (specify)

Application Data Sheet, See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

Applicant claims small entity status. See 37 CFR 1.27.

FILING FEE
AMOUNT (\$)

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80.00

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The invention was made by an agency of the United States Government or under a contract with an agency of the
United States Government.

No.

Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE Robert L. McKellar

Date 09-12-03

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REGISTRATION NO.
(if appropriate)
Docket Number:

26,002

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MSB - 269P

PTO did not receive the following
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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)

Applicant(s): Melvin Cabey and David E. Graham

Serial No.	Filing Date	Examiner	Docket No.	Group Art Unit
	<u>Sept. 12, 2003</u>		<u>MSH - 269P</u>	

Invention: DETERRING THE FORMATION OF CRYSTALLINE HYDRATES IN GAS AND OIL SYSTEMS

I hereby certify that the following correspondence:

new patent application consisting of 6 pages of specification, 1 page of Abstract, Provisional application cover sheet, return receipt postcard, Application data sheets.

Is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Commissioner for Patents P. O. Box 1450, Alexandria, Va. 22313-1450

Date: September 12, 2003

Robert L. McKellar

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Robert L. McKellar

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Be it known that We, Melvin A. Cabey, a resident of Midland, County of Midland, State of Michigan, and David E. Graham, a resident of Long Valley, County of Morris, State of New Jersey, a citizen of the United States of America and a citizen of the United Kingdom, respectively, have invented new and novel compositions and processes for

5 DETERRING THE FORMATION OF CRYSTALLINE HYDRATES IN GAS AND OIL SYSTEMS

the following of which is a specification therefore.

BACKGROUND OF THE INVENTION

The invention disclosed and claimed herein deals with compositions that deter the formation of crystalline hydrates in various systems, most notably, gas and oil transmission pipeline systems. The compositions are comprised of carbon dioxide sorbing polymers that also have the capability of driving the formation of hydrate crystals into the polymeric matrix.

Crystalline hydrates can form in oil and gas pipelines carrying oil and gas if the chemical composition of the produced fluids includes water, either or both of ethane or methane with carbon dioxide and sometimes, other hydrocarbon gases and/or sulfur dioxide. In addition to the chemical composition, there is a need for a driving force for such hydrate nucleation involving the physical and environmental conditions.

The fluid composition generally is at an elevated temperature, typically above 70°C and it will cool to a lower temperature, typically below 16°C, whereby the gases and water become super saturated and crystallize from solution at the lower temperature. The pipeline linking the sub-sea oil producing well to the processing platform is the crucial environment for the formation of the hydrate crystals. The surrounding seawater with temperatures that are about 4°C to about 6°C cools the pipeline that is carrying the produced fluids and obviously, the oil or gas contained therein.

Many years ago, when fluids were produced directly onto the production platform and arrived there at high temperatures, hydrates did not occur since the temperature of hydrate formation was typically between 15°C and 22°C. When the fluids arrived on board the processing plant at 25°C to 40°C the hydrate formation was not an issue. But, as oil fields became larger and more diverse and the use of sub-sea producing wells became

1 the normal practice, fluids produced therefrom would be cooled by the 4°C to 6°C
seawater around the sub-sea pipeline. Such situations were optimal for crystal hydrate
formation.

5 One of the main reasons for dealing with crystalline hydrates at all stems from the
fact that the hydrates are mixtures of water, methane, ethane, carbon dioxide and sulfur
dioxides, and these materials combine under ideal pressure and temperature conditions.
These solid hydrates, once formed, will grow in size to eventually plug flow lines, and in
some instances, once formed, travel through the pipelines at such velocities that they
become dangerous projectiles having high potential to puncture holes in the pipe line.

10 Thus, the formation of hydrates is a costly and potentially environmental
challenge for the oil and gas industry. As global offshore deepwater mining of oil and gas
increases, the challenges of preventing or diminishing the formation of hydrates remains
the industry technical challenge.

15 Prior art methods for deterring the formation of hydrate crystals in pipelines
include the continuous injection of methanol, ethanol, or glycol; offshore dehydration of
the gas so produced; warming fluids under normal flow conditions through insulation;
heating flow lines, and using low doses of chemical inhibitors for threshold hydrate
inhibition, kinetic inhibitor polymers, surfactants and emulsions, and anti-agglomerate
polymers and surfactants.

20 Of these, methanol, ethanol and glycol are currently practiced but the
environmental and financial costs are high. Methanol and glycols are added to pipeline
fluids at about 30 to 50% by weight of water co-produced. The costs are high but the
logistics for supply and storage offshore and more importantly pumping to sub-sea
producer wells are significant and cumbersome.

25 Offshore dehydration is not feasible for production from sub-sea producing wells
and the strategic option for warming the pipeline by heated water or other fluids from the
processing platform requires double wall pipeline, that is both expensive and logically,
a difficult operational process. Heating the flow lines when sub-sea is also expensive and
logistically problematic and flawed with respect to reliability. The low dose chemical
30 inhibitor is the new area and is currently under examination by a range of chemical
suppliers trying to develop low cost and high performance inhibitors

The threshold and kinetic inhibitors function to prevent the growth of hydrate crystals and act essentially like salt acts to depress the freezing point of water. However, the tolerance is not as great as the industry requires and fail in the majority of demanding situations. These are typically surfactants and polymers such as polyvinyl pyrrolidone or 5 polyvinyl pyridine, or polyvinyl caprolactum.

THE INVENTION

The polymers disclosed herein are chelating polymers capable of complexing with charged gaseous molecules such as the carbon dioxide by removing the carbon dioxide or more practically by scavenging for the carbon dioxide to prevent the methane or ethane 10 hydrate structures from forming since they require carbon dioxide to stabilize their structures.

The solid substrates are any solid substrates that are particulate, that in the case of embedding in the polymer, will embed in the polymer, and in the case of immobilization of the polymer, will allow the polymer to immobilize thereto.

15 The solid particle substrates can be hydrophobic or hydrophilic in nature, and examples of such materials are silica, silica gels, diatomaceous earth, sand, cellulosics, and the like.

Thus, there is a need for an economical, highly efficient process for preventing 20 the formation of crystalline hydrate crystals in various systems, such as gas and oil production and the invention provides such a process, along with novel materials for carrying out the process and making it highly effective.

What is disclosed and claimed herein is a composition of matter comprising 25 a carbon dioxide sorbing polymer of at least 5,000 gms/mole molecular weight and, a solid particulate material, wherein the carbon dioxide sorbing polymer has the capability of complexing the driver of the hydrate crystals into the polymer matrix.

Another embodiment of this invention is a method of deterring the formation of crystalline hydrates in a fluid system, wherein the method comprises contacting carbon dioxide in the system with a carbon dioxide sorbing composition.

With more specificity, the invention deals with polymeric materials that are 30 dendritic in nature, or are hyperbranched polyamino polymers wherein the polymers can be used in any one of several combinations.

For example, the polymers can be siliconized hyperbranched or dendritic polyamino polymers in solvent solution wherein the siliconization is that obtained by treating the polyamino polymers with reactive silanes, or silicones containing functional groups that will allow the polyamino polymers to combine with them.

5 Another example is the use of polyamino hyperbranched or dendritic polymers that have solid particles embedded in them, the solid particles being described *infra*. Yet another example of the use of the polyamino hyperbranched or dendritic polymers is one in which the polyamino hyperbranched or dendritic polymer is immobilized onto solid particle support, wherein the solid supports are those described *infra*.

10 Still another example is the use of the polyamino hyperbranched or dendritic polymers in a particular solvent solution, and finally, another example is the use of the polyamino hyperbranched or dendritic polymers in an emulsion form.

15 Polyamino hyperbranched or dendritic polymers, including those that are siliconized, are known in the prior art and there are many publications describing them and the methods for their preparation.

20 The polymers disclosed herein are chelating polymers capable of complexing with charged gaseous molecules such as carbon dioxide, by removing the carbon dioxide. More practically, the polymers scavenge for the carbon dioxide and thus, prevent the methane or ethane hydrate structure from forming, since they require carbon dioxide to stabilize their structure.

“Sorbing” for purposes of this invention means that the polymers have either an absorption, or an adsorption characteristic.

25 The solid substrates useful herein are any solid substrates that are particulate. In the case of embedding in the polymer, such particles must be capable of embedding in the polymer, and in the case of immobilization of the polymer, will allow the polymer to immobilize thereto. Where the composition is used that requires the particle to be embedded, up to about 80 weight percent of particles, based on the weight of the polymer can be embedded. On the other hand, in the case of the immobilization of the polymers on the substrate, up to about 80% of the polymer can be immobilized on the substrate, 30 based on the weight of the solid substrate.

The solid particle substrates can be hydrophobic or hydrophilic in nature, and examples of such materials are silica, silica gels, diatomaceous earth, sand, cellulosics, and the like. The relative size of the particles is not overly critical and any size from nano size through macro size can be used, with the understanding that smaller particles find a wider application in this invention.

5 Example 1

A standard commercial glass Pasteur pipette was held such that the pipette tip projected 12 cm from the stop bung. A drop of water was taken into the pipette by means of capillary suction and the pipette with the stop bung intact was weighed and then 10 cooled for at least 2 hours at -20°C in a refrigerator.

A 3.5% by weight sodium chloride solution was mixed with tetra hydrofuran in the ratio of 100: 25. A 50 ml. aliquot of this solution was added to a test tube of about 3 cm diameter and about 15 cm long that was held in a cooling bath at -1°C such that the test tube was immersed in the cooling bath to a depth of about 6 cm.

15 The frozen pipette was removed from the refrigerator, wiped rapidly to remove any crystal nuclei from the outside of the pipette in order to obtain standard initial conditions, and immediately immersed to a depth of about 1.5 cm in the 50 ml aliquot of the tetrahydrofuran/water/sodium chloride mixture. It became clear that within a very short period of time of between seconds to a couple of minutes, the tetrahydrofuran 20 hydrates began forming at the glass pipette tube surface.

The pipette was very carefully removed from the test tube after 60 minutes and the pipette with cork stopper and adhering hydrates were immediately weighed again. The difference in weight was attributed to hydrate crystals. The growth rate of the THF 25 hydrate formation in g/h can be calculated from the difference between the initial and final weights, and the time elapsed.

Examples 2 to 10

The protocol was identical to that carried out under Example 1, except that 2500 ppm of the corresponding inhibitor was added to the test solution unless stated otherwise. The simple evaluation was carried out identically to that set forth in Example 1 above. 30 The test thus used the same protocol as above with the hydrate anti-agglomerate additives shown in the table below. Examples 2 to 5 correspond to the prior art whereas Examples

6 and 7 relate to the process substrates without hyperbranched polymer coating and Examples 8 through 10 relate to inhibitors designed according to this invention that are silica substrates that have the polymer immobilized on the surface.

		Concentration	Hydrate Growth Rate	
	<u>Example #</u>	<u>Inhibitor</u>	<u>ppm by weight</u>	<u>gm/hour</u>
5	1	Nil	Nil	25
	2	methanol	2500	24
	3	isobutanol	2500	10
	4	2-butoxyethanol	2500	4.6
	10	5 2-isobutoxyethanol	2500	1.2
	6	90 micron silica	2500	25
	7	20 nm silica	2500	20
	8	90 micron silica + 10% hyperbranched polymer	2500	1.1
15	9	20nm silica + 10% hyperbranched polymer	2500	
	10	20nm silica + 10% hyperbranched polymer	1250	1.2
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ABSTRACT

Polymer compositions that deter the formation of crystalline hydrates in various systems, most notably, gas and oil transmission pipeline systems. The polymers are chelating polymers capable of complexing with charged gaseous molecules such as 5 carbon dioxide, by removing the carbon dioxide, or more practically by scavenging for the carbon dioxide, to prevent the methane or ethane hydrate structures from forming since they require carbon dioxide to stabilize their structures.

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APPLICATION DATA SHEET

APPLICATION TYPE:

Provisional

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deterring formation of hydrates

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DETERRING THE FORMATION OF CRYSTALLINE
HYDRATES IN GAS AND OIL SYSTEMS

ATTORNEY DOCKET NUMBER:

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